X-RAY POWDER DIFFRACTION: PROBLEMS AND PROSPECTS

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Abstrac: The methodology of structure solution from single crystal X-ray diffraction data is fairly well developed and unless twinning or severe disorder prevailing in the structure and it can easily solve structures of small and medium sized molecules. An intrinsic limitation of the technique, however, is the requirement to prepare single crystals of sufficient size and quality, which are not always met for all organic, inorganic and biological systems in the chosen crystal growth conditions and also within a reasonable time scale. In such circumstances, it is essential that structural information can be obtained from powder diffraction. This article highlights some recent developments in the field of *ab-initio* crystal structure determination from X-ray powder diffraction data. The different stages involved in structure determination using X-ray powder diffraction data and relevant fundamental aspects of different steps of structure determination procedure from powder data have been described with particular emphasis to the challenging structure solution stage.

***Key words* – X-ray powder diffraction, *ab-initio* crystal structure determination, Rietveld Refinement**

1. INTRODUCTION

X-ray diffraction is undoubtedly the most important and powerful technique for characterizing the structural properties of crystalline solids. Advances made over the past decade in structure determination from powder diffraction data are reviewed with particular emphasis on algorithmic developments for example, from high temperature superconductors to fullerenes, from nano technology to macromolecular crystallography, have relied heavily on this technique. Although single-crystal and powder-crystal diffraction patterns contain the same basic information, in the former case this information is distributed in three-dimensional space, whereas in the latter case the three-dimensional diffraction data are compressed into one dimension (**Fig. 1**). This leads to a considerable overlap of peaks in the powder diffraction pattern. Such peak overlapping obscures exact information of individual intensity of diffraction maxima in a powder pattern and appears as the main hurdle in *ab-initio* structure solution from X-ray powder diffraction. It is important to recognize that *ab-initio* structure determination from X-ray powder diffraction data is a far more complex task and significant challenges must be overcome at every stage in this endeavour. Considerable progress in the scope and potential of techniques for ab-initio structure solution from laboratory X-ray powder data has been made in recent years [1-4]. The present article gives an overview of the problems and challenges associated with structure determination from X-ray powder diffraction data. More detailed reviews covering all aspects of structure determination from powder diffraction data can be found elsewhere [5-7].

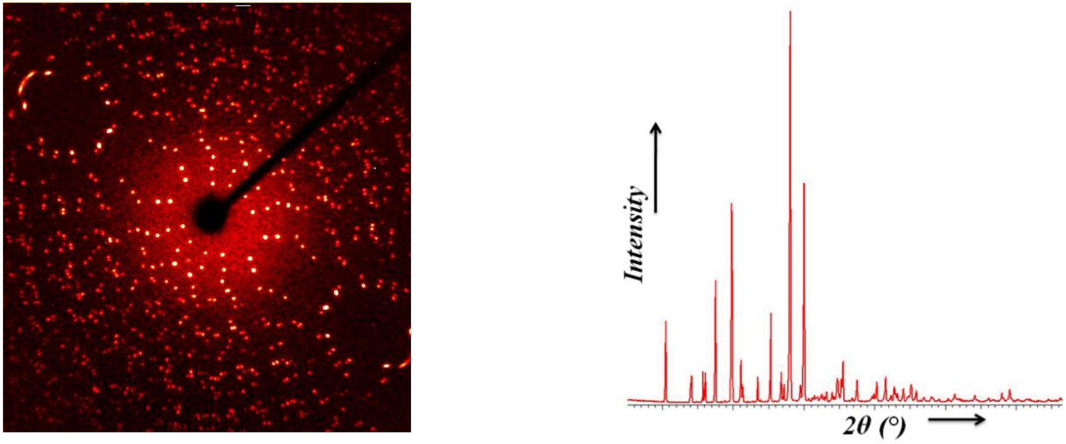

Fig. 1: Single crystal (left) and Powder (right) X-ray diffraction pattern.

2. GENERAL STAGES OF STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA

Crystal structure determination from powder diffraction data is generally divided into a series of steps, though there may be considerable overlap between different steps:

(i) Sample preparation and data collection
(ii) Indexing
(iii) Powder pattern decomposition
(iv) Space group assignment
(v) Structure solution
(vi) Structure refinement

For determining the unit cell parameters, only peak positions in the observed diffraction pattern are needed, whereas the assignment of space group, structure solution, and structure refinement require consideration of relative intensities of different diffraction maxima. In the structure solution stage, the aim is to derive an approximate model structure without any prior knowledge of arrangement of atoms, ions, or molecules in the unit cell. If the model structure is a good representation of actual structure, a good quality crystal structure can be obtained by refining of the structural model against experimental powder diffraction data. Non-equivalent reflections for which the peak positions (i.e. 2θ values) are sufficiently close to each other give rise to accidental overlapping and this is prevalent at high diffraction angles, and can be particularly severe for low symmetry structures, whereas well defined groups of nonequivalent reflections with identical peak positions due to symmetry are responsible for systematic overlapping. The resulting ambiguity in powder diffraction data thus creates particular problems in determining the unit cell parameters and subsequent extraction of integrated intensities for a sufficiently large number of reflections. Indeed, all parts of structure solution process from powder diffraction data are less straightforward than their single-crystal counterparts. The refinement of crystal structures using powder diffraction data can be carried out fairly routinely by the Rietveld profile refinement technique [8,9]. A schematic overview of different stages of structure determination from powder diffraction data is shown in **Fig. 2.**

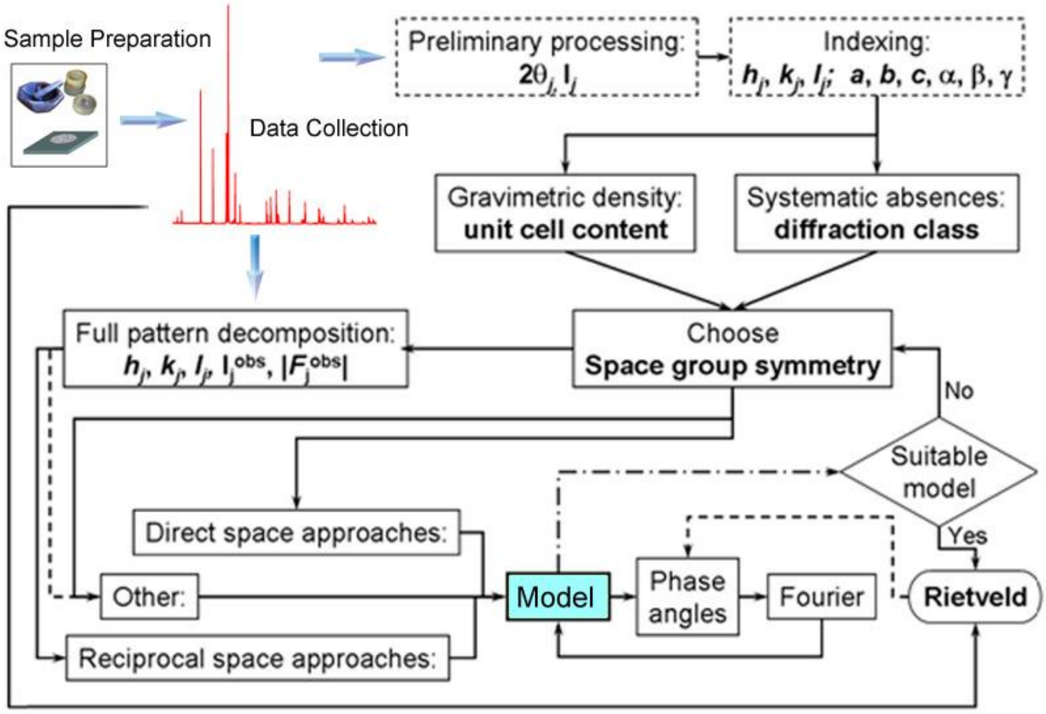

Fig. 2: Schematic diagram of structure solution procedure from Powder X-ray diffraction

3. EXPERIMENTAL CONSIDERATIONS

A pre-requisite for crystal structure determination from powder diffraction is the availability of good quality data from the material to be investigated. Although, synchrotron X-ray powder diffraction data are clearly preferable due to substantially improved signal / noise ratio and higher resolution. The majority of crystal structures determined till date using powder diffraction methodology have been obtained from conventional laboratory-based X-ray diffractometers. The relative merits of different X-ray optics used for powder data collection have been discussed in several reviews [10,11].

3.1: Sample preparation and data collection

Sample preparation for the structure determination from X-ray powder diffraction data (SDPD) is an important step, specially when the grain size is variable. An ideal powder diffraction pattern can only be obtained from a specimen containing an infinite number of crystallites with truly random orientations in the irradiated volume. The specimen should have a completely random distribution of crystallographic orientations of grains or crystallites. The powder material should be properly ground using a pestle and mortar or be milled to uniform grain size. Sample thickness and homogeneity play significant roles in getting a good quality powder diffraction pattern. Presence of impurities or multiple polymorphs in the sample is another hurdle, which can prohibit *ab-initio* structure solution. Indexing of two or more unknown phases from a single diffraction pattern is a non-trivial task. To assess the phase purity of the sample, chemical, spectroscopic (UV-Vis, IR, NMR) and mass spectral data are very useful and a priori knowledge of the molecular formula can often be obtained from these data.

When the sample for a powder diffraction experiment has been properly prepared, the next step is data collection. Although synchrotron radiation can provide good quality powder data in terms of intensity and resolution, most of the works are carried out with laboratory X-ray powder data measured on a modern X-ray powder diffractometer. X-ray powder diffraction data sets are usually collected in 2θ angular ranges 5°–100° in steps of 0.02° (or 0.01°) with counting time 20-25 seconds per step using $CuK_{\alpha1}$ radiation (λ=1.54056Å). For structure determination, use of primary beam monochromator is recommended because it gives sharper peaks without any $K_{\alpha 2}$ component, which is important for indexing. Due to inherent atomic scattering factor fall off with increasing scattering angle, the X-ray powder diffraction profiles in most cases become flat in the high angle region ($2\theta > 75°$). A 'variable counting time' (VCT) strategy can be useful for such situations. Of the various geometries developed for data collection, the Bragg-Brentano, Debye-Scherrer and Seemann-Bohlin parafocusing systems are most common in practice. All powder data presented in the thesis have been collected on a Bruker D8 Advance diffractometer with the Bragg-Brentano geometry (**Fig. 3**).

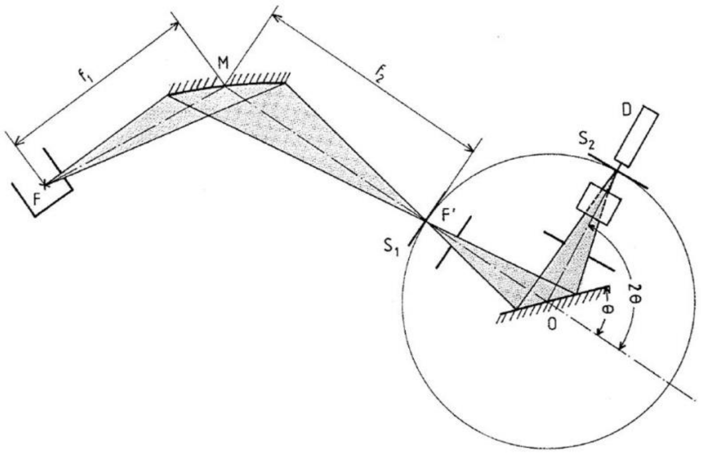

Fig. 3: Geometry of the Bragg-Brentano powder diffractometer with a conventional X-ray source (F) and incident-beam monochromator (M), short focal distance f_2 and focusing point F´. O is the diffractometer axis, D the detector and S_2 is the receiving slit. S_1 is an optional slit at F´.

3.2: Indexing of powder pattern

An essential prerequisite for crystal structure determination from powder diffraction data is that the lattice parameters and space group are known. Successful indexing of a powder pattern requires a knowledge of peak position (i.e. 2θ), which are normally obtained using a peak-search program, provided other systematic errors have been eliminated. Once the data set has been collected, individual diffraction peaks are fitted with appropriate profile functions to provide accurate 2θ positions of first 25-30 lines. Several auto-indexing programs such as, ITO [12], TREOR [13], DICVOL [14], NTREOR [15,16], McMaille [17] and CRYSFIRE [18] are available for indexing a powder pattern.

The basic equation used for indexing a powder diffraction pattern and determination of unit cell parameters is

$$\begin{aligned} Q_{hkl} &= 1/d_{hkl}^2 \\ &= h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* + 2hlc^*a^*\cos\beta^* \\ &\quad + 2hka^*b^*\cos\gamma^* \end{aligned}$$

where, d_{hkl} is the interplanar spacing corresponding to (hkl) plane and a*, b*, c*, α*, β*, γ* are the reciprocal lattice cell parameters. In general, auto-indexing programs generate several possible sets of lattice parameters that are consistent to a greater or lesser degree with a set of measured 2θ positions. To assess the reliability of indexing, two figures of merit, M_{20} [19,20] and F_N [21], are normally calculated.

The figure of merit, M_{20}, is defined as

$$M_{20} = \frac{Q_{20}}{2|\Delta Q|_{20}} \cdot \frac{1}{N_{20}}$$

where, Q_{20} is the Q value for the 20th observed diffraction line and N_{20} is the number of possible diffraction lines that could be observed up to Q_{20}.

The figure of merit, F_N, can be defined as,

$$F_N = \frac{1}{|\Delta 2\theta|} \cdot \frac{N_{obs}}{N_{poss}}$$

where, N_{poss} is the number of possible lines up to the N observed lines. From a consideration of respective merits of M_{20} and F_N, it was pointed out that F_N is more appropriate for evaluating the quality of a powder diffraction data set, whereas M_{20} is preferable for the indexing purpose. Higher the accuracy of data collection and more complete the observed diffraction pattern, larger will be the M_{20} and F_N values.

3.3: Space group assignment

The space group determination can often be ambiguous and sometimes it is impossible due to high degree of overlap in the powder diffraction data. In some cases, the space group can be determined by careful inspection of systematic absences in the intensity data. If it is not possible to assign the space group uniquely, structure solution should be attempted separately for each of the plausible space groups. In recent years, some new probabilistic approaches have been reported to overcome this problem [22,23]. An useful algorithm based on probabilistic approach has been implemented in the EXPO-2009 [24], which could statistically analyze the single diffraction intensity, decomposed from the original powder diffraction pattern and provide a probability value for each extinction symbol compatible with the existing lattice symmetry.

3.4: Powder pattern decomposition and extraction of integrated intensities

The extraction of integrated intensity from powder diffraction pattern is a critical step for solving crystal structures from X-ray powder diffraction data using the reciprocal space based methods. Due to overlapping of diffraction peaks, non-uniform background and possible preferred orientation, extracted integrated intensities are often inaccurate and the success of *ab-initio* crystal structure determination via Patterson or Direct methods is related to the quality of extraction of intensities. In a pioneering work, David [25] (1987) described two techniques for assigning integrated intensities to completely overlapping reflections.

The pattern decomposition can be accomplished by generating the profile in terms of analytical functions or convolution of analytical functions such as, Gaussian, Lorentzian, pseudo-Voigt and Pearson-VII functions [26]. In the Pawley method [27], the sum of the squares of differences between the observed and calculated profiles is minimized, and a set of parameters is refined by a least-squares technique, which includes the integrated intensities, unit cell dimensions, and parameters for modelling the background and peak shape. The Le Bail method [28] is an iterative process based on the Rietveld formula. The main drawback of Le Bail approach is that it assigns equal intensities to completely overlapping reflections.

3.5: Structure solution

Structure solution from X-ray powder diffraction data is the most challenging part among the various stages discussed so far. The techniques commonly used for structure solution from powder diffraction data can be subdivided into two categories- ‘reciprocal-space’ and ‘direct-space’ approaches. A priori knowledge of the content of the asymmetric unit from the unit cell volume, space group, density consideration, and other physical and chemical property measurements would facilitate the structure solution procedure.

In the traditional approaches (i.e. the Patterson or Direct methods) for solving crystal structure from powder diffraction data, intensities of individual reflections (I_{hkl}) are extracted from the experimentally observed powder pattern and then use them as input in the structure solution programs. The efficiency of Patterson or Direct method is, however, strongly depends on the quality of extracted intensities. For molecular crystals with large unit cell volume, low symmetry and more than one molecule in the asymmetric unit, structure solution attempts from powder diffraction data using traditional approaches are unlikely to be successful. The Patterson method is sometimes able to derive an approximate structural model from powder diffraction data provided the structure contains a small number of dominant scatterers or a structural fragment of well defined geometry. In recent years, algorithm based on traditional direct methods, specifically tailored for analysis of powder diffraction data, have been used quite successful. The best known program package for this purpose is EXPO2004 [24] which has been successfully used to solve several organic [29,30], organometallic [31], and inorganic crystal structures [32].

Due to difficulties encountered during application of traditional methods for solving crystal structures of moderate complexity from X-ray powder diffraction data, alternative structure solution strategies, the so called direct-space methods, have been developed. In the direct-space approaches [33-35], the molecular model of the compound whose structure to be determined is moved randomly in the already known unit cell, thereby generating trial structures in the direct space, independently of experimental X-ray powder pattern. The suitability of each trial structure is assessed by a comparison between the calculated powder pattern based on the trial structure and the observed powder profile. The comparison between the experimental and calculated powder patterns is usually monitored by the weighted profile R-factor, R_{wp} (defined in Table 1).

Table 1: Different parameters used in structure determination from X-ray powder diffraction

$R_p = \sum\|y_i\ (obs) - y_i\ (calc)\|/ \sum\ (y_i\ (obs)$	R-pattern (profile)
$R_{wp} = \{\sum w_i\ \|(\ y_i\ (obs) - y_i\ (calc))^2\ \|/\sum w_i\ (yi\ (obs))^2\ \}^{1/2}$	R-weighted pattern (profile)
$R_F = \sum\|(I_K\ (obs))^{1/2} - (I_K\ (calc))^{1/2}\ )\|/\sum(I_K\ (obs))^{1/2}$	R-structure factor

The basis of all direct-space methods is a global optimization problem of great complexity in which the agreement between the calculated and observed diffraction patterns is maximized. This is equivalent to exploring a hypersurface by varying the structural variables in order to find its global minimum. Many different global optimization methods like the simple Monte Carlo [35], genetic algorithms [36-38], evolutionary strategies [39], and particle swarm [40] have been explored in recent years. But it is simulated annealing [41,42] that is most popular due to the fact that it is an extremely effective algorithm and is also easy to use. In order to improve the efficiency of basic annealing algorithm, modifications such as parallel tempering [43], have also been implemented [44,45].

3.6: Rietveld refinement

The final stage in structure determination procedure from X-ray powder diffraction data, the structure refinement is carried out by the Rietveld method [46-48], which considers every data point in the powder diffraction profile as an individual intensity measurement. The powder profile is calculated on the basis of different individual and global parameters (Table 2).

Table 2: Parameters refinable simultaneously

For each phase present:	**GLOBAL**
x_j y_j z_j B_j N_j (x_j, y_j and z_j are position coordinates, B_j is an isotropic thermal parameter, N_j and is the site occupancy multiplier, all for *j*th atom in the unit cell)	2θ-Zero
Scale factor	Instrumental profile
Specimen-profile breadth parameter	Profile symmetry
Lattice parameters	Background
Overall temperature factor (thermal parameter)	Wavelength
Individual anisotropic thermal parameters	Specimen displacement
Preferred orientation	Specimen transparency
Extinction	Absorption

The quantity minimized in the least-squares refinement is the residual, S_y:

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

$$y_{ci} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi}$$

where, $w_i = 1/y_i$

y_{ci} = calculated intensity at ith step y_i = observed intensity at ith step

s = scale factor   K = Miller indices, h,k,l for a Bragg reflection

A = absorption factor L_K = Lorentz, polarization and multiplicity factor

ϕ = reflection profile function F_K = structure factor for Kth Bragg reflection

y_{bi} = background intensity at ith stepP_K = preferred orientation function

Exhaustive discussions on various aspects of Rietveld refinement are available in various texts and review articles [49-51]. For a successful Rietveld refinement, the initial structural model obtained from a structure solution protocol should be sufficiently close to the correct structure. Since the experimental X-ray powder diffraction data are affected by various errors due to inhomogeneity in sample preparation, nonuniform background profile, degree of preferred orientation etc., various geometric constraints or restraints are usually applied during the refinement stage. Convergence in the refinement process can often be accomplished by using a second data-set with increased number of observations [52,53] or reducing the number of refinable parameters via a rigid-body approximation [54]. The problems in refinement arising due to preferred orientation in polycrystalline materials can be minimised by using different available options i.e. the Rietveld-Toraya function [55], the March model [56], and generalized spherical harmonic [57-59].

4. CONCLUSIONS

The techniques and methods presented here have demonstrated the feasibility of solving crystal structures from laboratory X-ray powder diffraction data and have illustrated the scope and limitations of the methods that are currently available. It is nevertheless important to emphasize that the process of structure determination from powder diffraction data is not a black-box technique, and considerable care must be taken in every stage, i.e. from data collection to final structure refinement, to ensure the correctness of the derived structure model. Continuous advances in the capabilities and efficiencies of techniques used during different stages of structure-determination procedure, coupled with improved data-collection strategies and the speed of computers for data analysis promise an optimistic outlook for the field of crystal structure determination from X-ray powder diffraction data. The future development of indexing methodologies, space group assignment algorithms and optimization techniques will extend the application of powder diffraction in revealing new insights into structural properties of a wide range of materials including important biological systems, such as proteins, for which structural characterization by single-crystal X-ray diffraction technique is not possible.

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